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Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 0 882 813 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 09.12.1998 Bulletin 1998/50

(51) Int. Cl.⁶: **C23C 14/34**

(21) Application number: 98109210.9

(22) Date of filing: 20.05.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 02.06.1997 JP 157331/97

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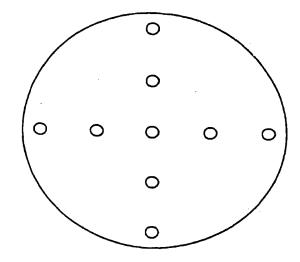
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(54) High-purity copper sputtering targets and thin films

(57) There is provided copper targets for sputtering capable of forming a deposition film with low electric resistance indispensable for high-speed operation elements and also with excellent thickness uniformity, and such thin copper films. A high-purity copper sputtering target is characterized by comprising up to 0.1 ppm each Na and K, up to 1 ppm each Fe, Ni, Cr, Al, Ca, Mg, up to 5 ppm each carbon and oxygen, up to 1 ppb each U and Th, and, excluding gaseous constituents, more than 99.999% copper. Preferably the average grain size on the sputter surface is 250 μm or below, with its dispersion within plus or minus 20%. I(111)/I(200) of X-ray diffraction peak intensity on the sputter plane is at least 2.4 with its dispersion within plus or minus 20%.





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[Background of the invention]

This invention relates to a high-purity copper sputtering target for the manufacture of thin film deposition materials. on semiconductors as in large scale integration and relates also to a thin high-purity copper films of low-resistivity obtained by sputtering with such high-purity copper sputtering target. See the control of the co

Aluminum or aluminum alloy (e.g., silicon-containing aluminum) has commonly been used as a wiring material for semiconductor integrated circuits and the like. However, such materials are presenting problems including increased resistance value and electromigration of wirings due to the recent tendencies toward higher degrees of integration which results further miniaturization of elements and the wirings. There have been some attempts to replace aluminum by a refractory metal such as molybdenum or tungsten, but their greater specific resistivities are a drawback.

Attempts have also been made to use copper in place of aluminum to take the advantage of its lower resistivity and greater resistance to electromigration. Nevertheless, pure copper can hardly be employed as a wiring material because it easily oxidizes and is highly reactive with silicon and silicon dioxide films. In the research for the development of copper wiring materials, therefore, emphasis has been laid on an improvement in the oxidation resistance of copper by the controlled addition of another specific element or elements. Most of the researches are directed to the coating of the resulting thin film with an oxide (or nitride) of the added element so as to prevent further oxidation of the film under the coat.

For example, Japanese Patent Application Kokai No. 64-59938 proposes a method which consists of depositing a wiring pattern of an alloy of copper and at least one element chosen from among Ti, Zr, Al, B, and Si, and annealing the deposited wiring pattern in a nitrogen-containing atmosphere whereby a substance that forms the alloy with copper is rion of all now need out of it details. diffused over the surface to form a nitride barrier.

Patent Application Kokai No. 6-177128 discloses a thin film wiring material of a copper alloy containing 0.02-20 atom% Al or Si. The alloy is oxidized to form an oxide film in which Allor Si is diffused and concentrated on the wiring surface so as to enhance the oxidation resistance of the surface. Subnociares of a content personal of the oxidation resistance of the surface.

A major problem common to the abovementioned methods is an increase in electric resistance by the addition of another element. An increased electric resistance retards signal transmission and adds to the power consumption. For this reason it has been necessary to put an upper limit to the proportion of the additional element so that the electric (S) bene tich ind Lo elephents euch as Fa, M, and Oc resistance is as low as that of pure Al, i.e., 2.7 μ Ω • cm or less.

As noted above, the efforts to make use of copper as a wiring material have depended largely upon the addition of a specific element, and few attempts have been made to use pure copper itself. However, the recent progress in device structures and barrier materials are altering the situation. For one things modern technologies including chemical mechanical polishing (CMP) have simplified device construction and enabled the use of devices with seemingly low oxidation resistance according to ordinary standards. For the other, the development of new barrier materials exclusively designed for copper has raised pure copper to a level high enough for practical use as a wiring material.

Under these circumstances the wiring deposition of pure copper that had been regarded as almost impossible is in may in the with them or leading action now rapidly gaining practicality,

In reality, however, the past scanty research on wiring deposition of pure copper has given little impetus to the study of the conditions required of copper wiring material; especially as a material for sputtering target. It should be pointed out, above all, that no copper sputtering target has been developed which has low enough electric resistance for the element that performs high-speed cperation for a computer of the like and which is capable of forming a thin film with element that percurity or so that the reputiting thin film shows an electric resistance below. Or the confidence that the excellent things are the confidence to the confidence between the confidence and the confidence that the

[Object of the invention]

Social seasons with an exact not year to or in elication has not negly to born too in action, a constant and elication. It is an object of the present invention to provide copper sputtering targets capable of forming wiring deposition films having excellent thickness uniformity as well as the low electric resistance essential for high-speed operation elements and also provide such thin copper films.

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[Summary of the invention] The rest of the state of the best best best best of the invention.

After an intensive research, the present inventors have now found that in order to produce a film of low enough electric resistance, the impurity contents in the target must be kept below certain numerical values. It has also been found necessary to limit down to certain levels the proportions of the elements that have been added for alloying purposes and, if the uniformity of film thickness is to be attained; the dispersions of grain size and crystalline orientation of the target must be controlled. 33 to 3 and many agent vs with accomplishment to street in motistic or no model in the On the basis of these findings, this invention provides no search in mile a notice year operators and include a trace of

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- 1. A high-purity copper sputtering target characterized by comprising up to 0.1 ppm each Na and K, up to 1 ppm. each Fe. Ni. Cr. At. Ca. Mg, up to 5 ppm each carbon and oxygen, up to 1 ppb each U and Th, and, excluding gaseous constituents, more than 99.999% copper.
- 2. A sputtering target according to 1 above wherein the average grain size on the sputter surface is 250 µm or below and the dispersion of the average grain size from location to location is within plus or minus 20%.
- 3. A sputtering target according to 1 or 2 above wherein the ratio, I(1,11) / I(200), of the X-ray diffraction peak intensity ((111) on the (111) plane to the X-ray diffraction peak intensity ((200) on the (200) plane is at least 2.4 and the dispersion of the ratio I(111) /I(200) in the sputter surface is within plus or minus 20%.
- 4. A sputtering target according to any of 1 to 3 above wherein X-ray diffraction peak width at half height in the sputter surface on the (111) plane is 20 ≤ 0.3 deg. asignapher impagations are the second second as a second s
- 5. A sputtering target according to any of 1 to 4 above wherein it also contains up to 5 ppm each Si, Ag, Ti, Zr, Hf, enum or tungstem, but their greater snecking resistanties's electravisealla.
- 6. A sputtering target according to any of 1 to 5 above wherein it has an electric resistance of 1.9μ Ω cm or less.
- A sputtering target according to an electric resistance of 2.0μ Ω cm or less produced by sput A thirr high-purity-copper film characterized by an electric resistance of 2.0μ Ω cm or less produced by sputtering with a high-purity copper sputtering target according to any-of t to 6 above.

restrained materials, their sure, amphasis has been laid on an improvement in the oxidation resisance or occapality. Brief explanation of the drawing percent of the rest of the rest satisfies are specified to the drawing percent of the specific of the rest and the rest and the rest and the rest are specified to the rest are spec enjoyed a for chiridon of the edded elections as to prevent further paids from of the tilm uniter the

FIG. 1 is a schematic view of a target, showing points of sampling for the investigation of its characteristics.

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The invention will now be described in detail.

The invention will now be described in detail.

The high-purity copper sputtering target of this invention has an impurity content reduced to a minimum.

In order to ensure the reliability of performance of a semiconductor device formed by sputtering, it is important to minimize the proportion of impurities deleterious to semiconductor devices. Particularly deleterious impurities include: to be settly dispresentational or a season and inscription and provide the control of the contro

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- (2) radioactive elements such as U and This and ito nothogong emiliations recourse may be a recourse of a second and the second as the second
- (3) transition metal elements such as Fe, Ni, and Cr.

tion! Items of supposed as a wiring material have depended largely upon the addition of

Alkali metal elements such as Na and K are especially diffusible and migrate easily through a insulation film, with the possibility of causing deterioration of MOS-LSI interface characteristics. Their proportions, therefore, should be limited to at most 0.1 ppm each, preferably 0.02 ppm eachdans but notioustance solve healthquizes (srt (50.5) on the Radioactive elements such as Usand Thremit alpha rays which can be responsible for soft errors of semiconductor

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elements. That is why their proportion should be severely controlled, to 1 ppb or less, preferably to 0.5 ppb or less, each. Transition metal elements such as Fe, Ni, and Cr too can cause troubles of interface connections. Hence their pro-

portions should be 1 ppm or less, preferably 0.1 ppm or less, each.

Besides these elements, particularly those harmful to semiconductor elements, other impurities must also be minimized. Generally, electric resistance is a function of the impurity level and the smaller the impurity content the lower the electric resistance. Thus, in order to lower the electric resistance, a higher purity is desirable. When the actual cost of producing a sputtering target and other considerations are taken into account, it would be of great practical value to control the impurity level so that the resulting thin film shows an electric resistance below 2.0 μ Ω • cm tranction 182

Thus not only the heavy metal elements but also such light metal elements as Al, Ca, Mg must be reduced in pro-

portions, to 1 ppm or less, preferably 0.1 ppm or less, each.

Gaseous ingredients such as carbon and oxygen too are undesirable in that they increase the electric resistance of the resulting film and have adverse effects upon the surface configuration of the film. The carbon is included herein as a gaseous ingredient since it is a gasifiable ingredient. Their contents should be kept to 5 ppm or less, preferably 1 ppm or less, each.

Research has suggested the desirability of minimizing also the proportions of Si, Ti, Zr, Hf, B, and Ag that have been often added as alloying elements, for the sake of reduced electric resistance. Their proportions should be 5 ppm or less, preferably 0.5 ppm or less, each.

The overall copper purity, excluding the gaseous ingredients, should be at least 99.999%.

For the uniformity in thickness of the film that is formed by sputtering, it is essential to restrict the dispersions of the crystalline grain size and orientation of the target memele entro anothogona entralevel misman

As for the grain size, both the average grain size in the sputter surface and the variation of the average grain size from location to location influence the uniformity of film thickness. If the average grain size is greater than 250 µm, it is no longer possible to limit the average dispersion of film thickness on an 8-in wafer to 2.0 or less. A locational variation

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in excess of 20% is undesirable either, because the average dispersion of film thickness exceeds 2.0 even though the ways first average grain size is below 250 µm. Thus, an average grain size in the sputter surface of 250 µm or below; and; a locational variation in the average grain size of not exceeding plus or minus 20% are requisites for the realization of film thickness uniformity.

On the other hand, crystalline orientation too has similar influences upon the uniformity of film thickness. The Joint Committee of Power Diffraction Standard (JCPDS) reports that a wholly random orientation gives an X-ray diffraction.

Deak intensity (1111)/I(200) = 2.08. Investigations by the present inventors, however, have revealed that intensified cries as the control of th

The sputtering rate depends on the plane of orientation. The sputtering rate thus varies from location to location where the orientation is at random, resulting in less uniformity of film thickness than with the orientation in a specific plane. In the case of copper, the (111) plane is the densest of its crystallographic planes, where the density of the sputtered atoms released is higher than in the other planes, leading to superior film thickness uniformity.

A work deformed layer of the target surface is another factor influencing the film deposition characteristic. The term "work deformed layer of the target surface" is used to mean a layer of the target surface with fractured crystallinity or microcracks and other flaws formed under the pressure of a cutting tool during machining (usually on a lathe). The presence of a work deformed layer is known to have unfavorable effects; e.g., instable deposition rate, increased film resistance, and inadequate film thickness uniformity. These effects can be avoided by presputtering the work deformed layer immediately before ordinary sputtering. The present inventors have improved the film deposition performance by machining each target in such manner as to minimize its deformed layer. Since the presence of a deformed layer expands the half width of X-ray diffraction, the present inventors estimated the volume of the deformed layer present from the X-ray diffraction peak width at half height. It has been found as a result that, if a favorable deposition performance is to be secured, it is necessary that the X-ray diffraction peak width at half height in the sputter surface on the (111) plane be 29 ≤ 0.3 deg.

Such a high-purity copper target with a minimized impurity content and outstanding film thickness uniformity as the described above can be made in the following way. One can be said the public state of the content of

Ordinary electrolytic copper is electrorefined in a bathlof sulfuric acid or hitric acid to reduce the impurity content, and the and attain a high-purity level of at least 99.9999%. The copper is then vacuum induction melted and a high-purity copper ingot is obtained. The ingot is hot worked by hot forging, hot rolling, etc., cold worked by cold rolling, cold forging, and the cold rolling cold forging, and the cold rolling cold forging, and the cold rolling cold forging and the cold rolling cold rollin etc., and then heat treated. Hot working to a working ratio of 50% or more, cold working to a ratio of over 30%, and heat treatment at 350-500°C for 1-2 hours are desirable. The hot working is indispensable for destroying the cast structure and refining and adjusting the ingot to a structure of equiaxed grains. Once the cast structure has been destroyed, cold working and heat treatment are carried out under strictly controlled conditions to refine the grain size and control the crystalline orientation. The cold working ratio influences the grain size after the heat treatment, and the greater the working ratio the finer will be the grains to be obtained. It is effective too in attaining a crystalline orientation as desired. Meanwhile, the material begins to harden owing to work hardening as the working ratio increases. The hardening beyond a certain level can cause cracking during the course of working. For these reasons the cold working ratio should be at most about 90%. The temperature and time for the heat treatment have certain bearings upon the grain size after ment about 90%. recrystallization. Proper choice of heat treatment conditions renders it possible to obtain a copper plate having a desired grain size. A too low temperature should be averted because it would effect insufficient recrystallization and and a promote the state of th produce a structure not thoroughly freed from working strains. Too high a temperature, on the other hand, induces grain growth which coarsens the crystal grains. The time for heat treatment has a less significant influence on the structure and, taking the productivity into consideration, a duration of one or two hours is adequate.

Following the heat treatment, the copper plate is lathed or otherwise machined to a target shape. The machining conditions must be carefully controlled since they dictate the formation of a deformed layer in the final product. Recommended lathing conditions are: turning velocity, 40-80 rpm; cutting tool feed, 0.1-0.2 mm; and depth of cut, 0.1-0.2 mm. Machining conditions are correlated with productivity, and high-speed operation is beneficial for productivity but can lead to the inclusion of a deformed layer. Hence the above-mentioned conditions are desirable. The copper plate that has been machined to a desired shape is then bonded to a backing plate and is ready for use as a sputtering target.

[Examples]

The invention is illustrated by the following examples and comparative examples. The invention is illustrated by the following examples and comparative examples 2-3, targets were made each from a high-purity copper ingot obtained by electrorefining an electrolytic copper in a nitric acid bath and then melting by vacuum induction. Comparative Examples 2-3, targets were made each from a high-purity copper in a nitric acid bath and then melting by vacuum induction. Comparative Examples and then melting by vacuum induction.

The above mentioned flar jets 7 to Ginertigram signs with dispersions and diffriction pusit introsity ratio.

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ple 1 represents a target made from a low-purity copper ingot. The targets were in the form of a disk each, measuring 12.98 in. inidiameter and 6:35 mm thick: a set or explication and his said near a general and a set or explication and his said near a set or explication and and purhasons to his near the group and his production.

(Example 1) Target A finished with the control of the process of rains and an expension of the control of the process of rains and the control of the contro

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Electrolytic copper was electrorefined in a nitric acid bath with anode and cathode separated by a partition film and was vacuum melited to make a high-purity copper ingot (157 mm dia, and 60 mm thick). The ingot was heated to 600°C and hot forged to dimensions 190 mm dia, and 40 mm thick. It was again heated to 600°C and rolled to 265 mm dia, and 20 mm thick. Following this, it was cold rolled to 360 mm dia, and 10 mm thick and then heat treated at 400°C for one hour. The work was lathed to a disk shape 12.98 in dia, and 6.35 mm thick, and the disk was bonded to a backing plate to complete a target. The conditions for lathing were: turning velocity, 70 rpm; depth of cut, 0.15 mm; and cutting tool feed, 0.12 mm. The conditions for lathing were turning velocity, 70 rpm; depth of cut, 0.15 mm; and cutting tool feed, 0.12 mm.

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The same ingot as used in Example 1 was hot rolled at 600°C to dimensions 300 mm dia. and 15 mm thick and then cold rolled to 360 mm dia; and 10 mm thick. The resulting plate was heat treated at 400°C for one hour, and under the same conditions as in Example 1, a target was made to heat a nation of beautiful and the same conditions as in Example 1, a target was made to heat a nation of beautiful and the same conditions as in Example 1, a target was made to heat a nation of the same region of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 1, a target was made to heat a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in Example 2, a nation of the same conditions as in the same conditions as in the same conditions as in the same condition of the same conditions as in the same condition of the same condi

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Starting with the ingot of Example 1y the process steps of Example 1 were followed down to cold rolling. The rolled plate was heat treated at 550°C for one hour and then subjected to the same machining conditions as in Example 1 to make a target? It is the process at the process steps of the same machining conditions as in Example 1 to make a target? It is the process at the process steps of the same as a target? It is the process at the process steps of the process

(Example 4) Target Depression of the strip of deal to allow washe or unartitle year. Year the frequency of the unartitle strip of the s

The same ingot as used in Example 1 was not forged, cold rolled, and not rolled under the same conditions of Example 1 to obtain a disk-shaped copper plate 360 mm dia, and 10 mm thick. This copper plate was lathed at a speed of 70 rpm, cut of depth of 0.4 mm and tool feed of 0.3 trum to the shape of a target.

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Pro in the state of the state of the control of 10% or more, sold working to a ratio of sver 30%, a working to a ratio of the copy of the copy of the copy of the copy of the ingot to a structure of a the copy of the ingot to a structure of a the copy of the copy of the ingot to a structure of a the copy of the copy of the ingot to a structure of a the copy of the

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(Comparative Example 2) Target-Fins at 1 and self-ratio asis mang and agonomical processing of mountains of mountains and processing and the first of the processing of the pr

The same ingot of the 99.95% purity as used in Comparative Example 1 (157 mm dia. and 60 mm thick) was not rolled at 600°C to a size 360 mm diacand:10 mm thick. Without a subsequent heat treatment, the work was lathed under the same conditions as in Example:11 to make a target at the make a starget at the make at a starget at a starget at a starget at a starget a

a griver staid responsibilities of eldisord if are one entitioned them taken to enterly required and the comparative Example 3) Target Griven better bloom if equated better and a continuance wood. A not a given and the continuance wood is not a property of the continuance of the

The ingot of the 99.95% purity as used in:Comparative Example 1 (157 mm dia. and 60 mm thick) was hot rolled at 600°C to dimensions 265 mm dia. and 20 mm thick and then cold rolled to 360 mm dia. and 10 mm thick. Without a heat treatment but under the same conditions as in Example 1 the work was lathed to a target.

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The provided all and the configurations and high-speed operation is beneficial for productivity but was served to be a ficial for productivity but was served to be a ficial for productivity but was served to be a finished in the configuration of a definition of a definition of the provided the provided to the configuration of the provided the provided to the provided the provid

operations of a deferrence of a deferrence the above-mentioned confe**blas interestant and resilinary mentioned** confeblas as a sputtering target.

Target characteristics

The above-mentioned Targets A to G had grain sizes with dispersions and diffraction peak intensity ratios of the (111) plane and the (200) plane with dispersions as shown in Table 2 estates a private that all you begin to the For the measurements of each target, samples were cut-out from a total of 9 points shown in FIG. 1. Grain sizes were determined by the scission method stipulated in UIS (Japanese Industrial Standards) H501

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Film deposition test

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ſ	Target	Unit:	Ex. 1 A	Ex: 2 B	Ex. 3 C	Ex:40D	⊕Comp. Ex. 1	E	Comp. Ex. 2	Comp. E	x: 3 G	5
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The high-printy cooper an flating tergit appareing to this invention is departs to the single of the single of et la lay on maistivity of no more than 2 use - ont and outstanding uniformity of film into listing diseased on the law to the absorbed aspignmenting to sink at the nursymmula to esercic at this at Concreily there is a relation

R = p + U/3 - F

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[Table 2]

Target (cities of)	Ex. 1 A	Ex. 2 B	Ex. 3 C	Ex. 4 D	Comp. Ex. 1 E	Comp. Ex. 2 F	Comp. Ex. 3 G	ا باداد ع
Grain size (μm)	150	200	460	150	120	250 ggas		385
Dispersion of average grain size (%)	1 ±14 11 1 acond:	±19	**± 28 **** ISTEM 2111	no bersiur	im thickness acci	un is meant the	THE CONTRACTOR OF THE SECONDARY SECONDARY SECONDARY SECONDARY	
l(111)/l(200)	5.2	2.5	4.8	5.2	BAU 2 5.1 10 AU	UMACT1.5 NUT	0.5	
Dispersion of peak intensity ratio(%)	±11	±19	±14	±11	±13	±25	±21	3 ° ¥:
Half width (deg)	0.16	0.20	0.11	0.34	{7 a ·0.1/7	0.17	0.17	

* Comparative Example 3 inv				ŧ			
could not be measured.	\$0.0	10.0	800.0	600.0	8070	2.603	<u> </u>
\$3.4	6.05	60.0	3	:	i	•	1
£:)	0.6	Table 31	85.0	0	20.3	80.0	,

Target	Ex. 1 A	Ex. 2-B-	Ex 3 C-	_Ex. 4.D	Comp. Ex. 1.E.	Comp. Ex. 2 F	
Resist'y (μ Ω· • cm)	1.85	1.85	1.85	1.85 20.0	2.2 ±0.0		2.2 40 0
Thickness dis- tri.dispn o(%)	1.5 S	1.8	2.3	_1.5 ⊊	5 4.5 16.0	2.5 0.0	4.0 ,
Desposition thickness neces-	3	5	3	15	∂., 3 ,	د 3	3 7
sary for dummy		<i>j</i> :		á		*	
run* (μm)	8	a		5	0.1	.50	1.1.

* The thickness for dummy run means the deposition film \text{15ickness required to be accumulated until the dispersion of the film thickness distribution reaches the value given in Table 3: 10.0 (Results)

The films formed using the high-purity copper sputtering targets according to the invention had very low resistivities of no more than $2\mu\Omega \cdot cm$. ئا. ت

Excellent uniformity of film thickness distribution was exhibited by the films formed with the targets baving an average grain size of 250 µm or less, grain size dispersion within plus or minus 20%, X-ray diffraction peak intensity ratio, I(111)/I(200), of no less than 2.4, and peak intensity ratio dispersion within plus or minus 20%.

It was confirmed that the film thickness necessary for a dummy run may not be great when the film is deposited using a target with a peak width at half height in the (111) plane of less than 0.3 deg.

[Advantages of the invention]

The high-purity copper sputtering target according to this invention is capable of producing a copper film of extremely low resistivity of no more than 2 μ Ω \bullet cm and outstanding uniformity of film thickness distribution. Moreover, the film thickness of dummy run at the time of sputtering can be decreased.

Generally, there is a relation

R = μ · L/S

where R: resistance,

μ: specific resistivity,

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L: length, and

S: cross sectional area.

Thus, in the case of a film with a resistivity of no more than $2\mu \Omega \cdot cm$ made in conformity with this invention, the resistance can be kept low even after wire thinning.

Also, a relation

 $Q = I^2 \cdot R$

o where

Q :Joule heat, and

I : current

holds, and the current that flows being the same, the film evolves less Joule heat. Compared with a copper deposition film with a purity of 99.95%, a 99.9999%-pure copper film of the invention has a lower resistivity, by about 10%. Hence when the same circuit is made, according to the above equation, the film of this invention can reduce the quantity of Joule heat by about 10%.

Its low resistivity reduces the delay of signal transmission and effects a saving of power consumption.

Claims

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1. A high-purity copper sputtering target characterized by consisting of up to 0.1 ppm each Na and K, up to 1 ppm each Fe, Ni, Cr, Al, Ca, Mg, up to 5 ppm each carbon and oxygen, up to 1 ppb each U and Th, and, excluding gaseous constituents, more than 99.999% copper.

A sputtering target according to claim 1 wherein the average grain size on the sputter surface is 250 μm or below and the dispersion of the average grain size from location to location is within plus or minus 20%.

3. A sputtering target according to claim 1 or 2 wherein the ratio, I(111)/I(200), of the X-ray diffraction peak intensity I(111) on the (111) plane to the X-ray diffraction peak intensity I(200) on the (200) plane is at least 2.4 and the dispersion of the ratio I(111)/I(200) in the sputter surface is within plus or minus 20%.

4. A sputtering target according to any of claims 1 to 3 wherein X-ray diffraction peak width at half height in the sputter surface on the (111):plane is 20 ≤ 0.3 deg.

5. A sputtering target according to any of claims 1 to 4 wherein it also contains up to 5 ppm each Si, Ag, Ti, Zr, Hf, and

6. A sputtering target according to any of claims 1 to 5 wherein it has an electric resistance of 1.9μ Ω γ cm or less.

7. A thin high-purity copper film characterized by an electric resistance of 2.0μ Ω • cm or less produced by sputtering with a high-purity copper sputtering target according to any of claims 1 to 6.

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EUROPEAN SEARCH REPORT

Application Number

EP 98 10 9210

·	DOCUMENTS CONSIDE	RED TO BE RELEVANT	<u> </u>	
ategory	Citation of document with income of relevant passa		Relevant to claim	CLASSIFICATION OF THE APPLICATION (InLCI.6)
	DATABASE WPI		1-7	C23C14/34
,	Section Ch, Week 910	15		•
	Derwent Publications	Ltd., London, GB;		
	Class LO3, AN 91-032			
ì	XP002077424			· · · · · · · · · · · · · · · · · · ·
	-& JP 02 301586 A (FURUKAWA ELECTRIC CO		•
	LTD), 13 December 19	990 [*]		
	* abstract *	The second of th	कर ग्रद	
	0.540405 1107		1-7	
	DATABASE WPI	ne .	11-7	
	Section Ch, Week 910 Derwent Publications	us cita landan GB:		1
	Derwent Publications	5 Ltd., Edildon, GB,		
	VP002077425	2540 to 3811 (A.E. 10) 19	W D 43	N. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.
	-& JP 02 301585: A.()	FURŪKĀWA ELECTRIC≪GO 🚉	ITT C	
		990 , 3-8 (37) 774. 32		
	* abstract *	, , , C. 1 1 1777	` i	
		77	1	
	PATENT ABSTRACTS OF	JAPAN F 18 S S S S S S S S S S S S S S S S S S	1-7	
	vol. 018, no. 128 (C-1174), 2 March 1994	1	TOTAL SECTION OF THE
	-& JP 05 311424 A 4	(DOWA MINING CO LTD); '	Tana deci	SEARCHED (Int.Cl.8)
	22 November 1993	COUMA MINING CONCINDATION OF THE CONCINDATION		C33C
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	vol. 11, no. 6, Apr	11 1987, page 400		
	X UU2U// 422		- F	
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	The present search report has	been drawn up for all claims		
		Date of completion of the search	1: 1	Examiner
	Place of seeign	14 September 199	8 Pa	tterson, A
	CATEGORY OF CITED DOCUMENTS	Wind the Control of theory or princip	ole underlying the	invention : 1 1 1 1 1 1
	erticularly relevant if taken alone	E : earlier patent of after the filling d	ocument, but put ate	Hished on, or
Y : pa	irticularly relevant if combined with ano		in the application	n
do	current of the same category chnological background	L. document also		
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